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Key Points:
- First total P budget for peatland
- P is recycled in the shallow soil profile
- P is almost in equilibrium between inputs and outputs

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The total phosphorus budget of a peat-covered catchment

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Abstract Although many studies have considered the carbon or greenhouse gas budgets of peat ecosystems, only a few have considered the nutrient budget of peat soils, and this, in turn, has limited the ability of studies to consider the impact of changes in climate and atmospheric deposition on the phosphorus budget of a peat soil. This study considered the total phosphorus (P) budget of an upland peat-covered catchment over the period 1993 to 2012. The study has shown (i) total atmospheric deposition of phosphorus varied from 62 to 175 kg P/km^2/yr; (ii) the carbon:phosphorus ratio of the peat profile declines significantly from values in the litter layer (C:P = 1326) to approximately constant at 30 cm depth (C:P = 4240); (iii) the total fluvial flux of phosphorus varied from 49 to 111 kg P/km^2/yr, of which between 45 and 77% was dissolved P; and (iv) the total phosphorus sink varied from −5.6 to +71.7 kg P/km^2/yr with a median of +29.4 kg P/km^2/yr, which is within the range of the estimated long-term accumulation rate of phosphorus in the peat profile of between 3 and 32 kg P/km^2/yr. The phosphorus budget of the peat ecosystem relies on rapid recycling near the soil surface, and this means that any vegetation management may critically deprive the ecosystem of this nutrient.

1. Introduction

Within the terrestrial biosphere, the northern peatlands are the most important terrestrial carbon (C) store: *Gorham* [1991] has estimated that 20–30% of the global terrestrial carbon is held in just 3% of the land area. The northern peatland carbon store is estimated to be approximately 4.5 Gt C and over the Holocene northern peatlands have accumulated carbon at an average rate of 0.96 Mt C/yr, making this ecosystem not only a substantial store but also a large potential sink of atmospheric carbon [*Gorham*, 1991]. If the northern peatlands are a significant sink of carbon and it is humified plant matter that is being stored, then any sink of organic matter will also be a sink of nitrogen (N), oxygen (O), sulphur (S), and of phosphorus (P).

Although complete carbon budgets of peatlands are now common [e.g., *Worrall et al*., 2003a; *Billett et al*., 2004; *Roulet et al*., 2007; *Nilsson et al*., 2008] and a number of studies have begun to explore the impact of climate change and other external drivers upon the carbon budget [e.g., land management, *Clay et al*., 2010], there are fewer studies that have completed total nutrient budgets for peat soil systems. *Hemond* [1983] studied a New England bog and found that about one third of nitrogen input to the bog was "permanently" stored—amounting to 0.58 t N/km^2/yr, and *Worrall et al*. [2012] found that the contemporary total N budget of a peat ecosystem over a 17 year period and found that the total N budget varied from +1.0 ton N/km^2/yr (sink) to −2.5 ton N/km^2/yr (source), i.e., in some years the ecosystem was a net source of N, but found that long-term accumulation was between 0.4 and 19 t N/km^2/yr. Several studies have investigated N retention in peatlands without completing a total N budget [e.g., *Bowden*, 1987; *Urban and Eisenach*, 1988; *Verry and Timmons*, 1982; *Tauchnitz et al*., 2010]. Alternatively, *Moore et al*. [2004] measured the long-term accumulation of N in Canadian peatlands and showed rates of between 0.5 and 4.8 t N/km^2/yr. The contemporary P budget of a peat soil has not yet been considered. The contemporary budget will measure fluxes rather than accumulation in the case of P of an ombrotrophic bog this can thought of as the comparison of the atmospheric inputs versus the outputs via losses to the stream network. However, it is also possible that any mismatch between inputs and outputs can be balanced by changes in internal supply and in a peat bog accumulation in the long term (Figure 1).

There are studies that have considered components of the P budget of peatlands. *Bridgham et al*. [1998] considered P mineralization across a gradient of peatland types from ombrotrophic to minerotrophic bogs and found that although minerotrophic bogs had a high total P content, this was compensated for by a higher P mineralization rate in comparison to ombrotrophic bogs. *Wang et al*. [2012] calculated an accumulation rate

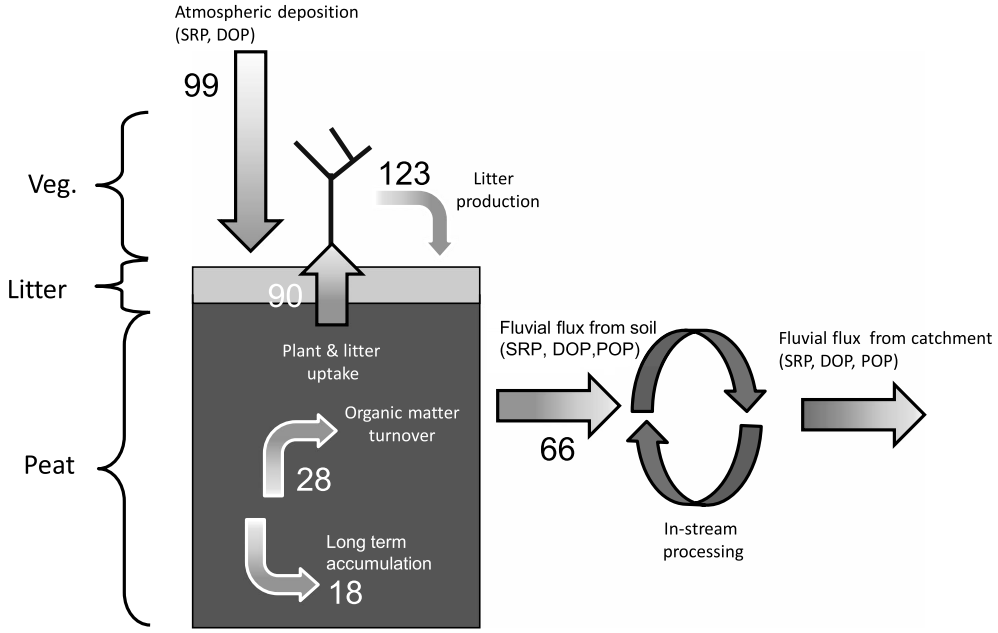

Figure 1. Schematic diagram of the P budget considered for this catchment. The values are the median P flux for the pathway in kg P/m^2/yr details of which are given in the text.

of total P in a Chinese peatland of between 0.69 and 2.04 t P/km^2/yr which was higher than that reported for a Michigan fen by *Richardson and Marshall* [1986]—0.2 to 0.5 t P/km^2/yr. Most recently, *Wang et al*. [2015] have estimated that average P accumulation in Canadian peats since the end of the last glaciation was 1.6 kg P/km^2/yr and suggested that such low accumulation suggested that P is rapidly recycled at shallow depths in the profile. *Schillereff et al*. [2016] have estimated the P accumulation rate for five UK peat bogs and found an average of 18 ± 4 kg P/km^2/yr. All published budgets are based upon long-term accumulation rate approaches [*Turetsky et al*., 2004], but these are a poor guide to contemporary processes as they can only reflect net accumulation and never periods of loss [*Worrall et al*., 2009]. Furthermore, contemporary budgets will reflect the influence of management, and many of UK's peatlands are under a range of increasing pressures from a changing climate and the land uses on them [*Reed et al*., 2009].

Therefore, the aim of this study was to estimate the total P budget for a peatland catchment to assess how much P is accumulating and the potential for nutrient status changes given ongoing pressures such as changes in land management or anthropogenic climate change.

2. Approach and Methodology

The external inputs of total phosphorus to an ombrotrophic bog are only as atmospheric deposition where total phosphorus includes inorganic and organic, dissolved, and particulate forms. The only exports of total P from the peat soils of the study catchment were fluvial and included orthophosphate (soluble reactive phosphorus—SRP), particulate organic phosphorus (POP), and dissolved organic phosphorus (DOP). Internal processing of P is considered as a result of the organic matter cycling processes, i.e., the release and uptake of P as organic matter decomposes. If the dry matter and carbon flows through the ecosystem are combined with knowledge of the P composition of the organic matter reservoirs and pathways, then the P cycling can be estimated. The schematic P budget is illustrated in Figure 1. Note that as an initial hypothesis it has been assumed that both litter and plant represents uptakes of P from the peat profile as this is the situation for N at this study site [*Worrall et al*., 2012].

The overall P export or flux was calculated for the combination of uptake and release pathways. By convention a negative flux was considered as loss of P from the peat soil and a positive flux was a flux to the peat soil. As calculated here this is an estimate for the peat soils of a whole catchment rather than just for a single peat profile or for the whole catchment, i.e., the study considers the streams of the catchment and any subpeat runoff

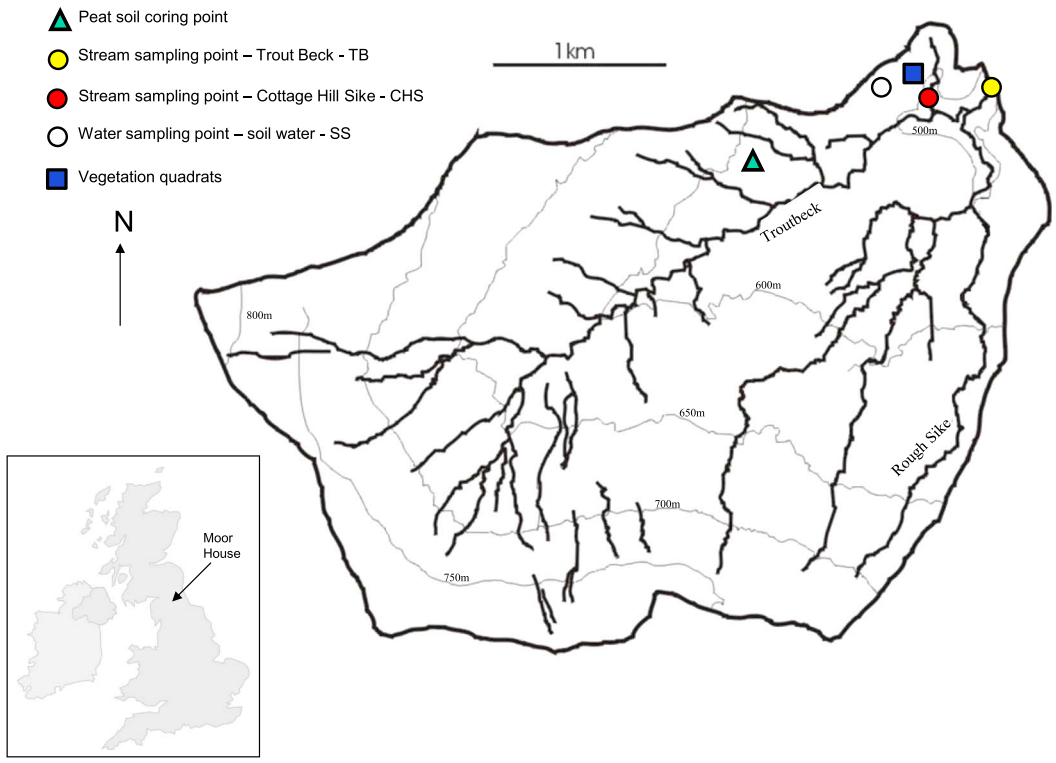

Figure 2. The location of the study catchment showing.

sources as separate. The error in the total P budget is assessed by the combination of the errors of each of the uptake and release pathways considered: 100 values were chosen at random from these ranges and combined. The resulting distribution of budgets was then examined to give the median and interquartile range.

2.1. Study Site

The Trout Beck catchment is an 11.4 km^2 blanket peat catchment in the headwaters of the River Tees (National grid ref. NY 756326, N54:41:18 W2:22:45; Figure 2). The study site lies within Moor House National Nature Reserve, a terrestrial and freshwater site which is part of the UK Environmental Change Network (ECN). The ECN collects various chemical and hydrological data from the Trout Beck catchment relevant to this study [*Sykes and Lane*, 1996].

The Trout Beck catchment lies largely above 500 m above sea level; the highest point is the summit of Great Dun Fell at 848 m above sea level. The underlying geology is a succession of Carboniferous limestones, sands, and shales with intrusions of the doleritic Whin Sill [*Johnson and Dunham*, 1963]. This solid geology is covered by glacial till whose poor drainage facilitated the development of blanket peat during the Holocene. Blanket peat covers 90% of Trout Beck catchment [*Evans et al.*, 1999]. The vegetation is dominated by *Eriophorum* sp. (cotton grass), *Calluna vulgaris* (heather), and *Sphagnum* sp. (moss).

The mean annual temperature (1991–2006) was 5.81°C; air frosts were recorded on 99 days in a year (1991–2006) [*Holden and Rose*, 2011]. Mean annual precipitation (1953–2006) was 2012 mm with the mean number of days with snow cover as 41 (1991–2006) [*Holden and Rose*, 2011].

2.2. External P Inputs

Precipitation samples included both wet and dry deposition and were analyzed for SRP and dissolved organic carbon (DOC). The samples have been taken weekly since January 1993. To obtain an annual deposition flux, the concentration data for each sampling period was combined with the volume of rainfall measured for the catchment from a rain gauge situated within the catchment that has been recording hourly rainfall since 1992.

The component flux in precipitation was estimated in several ways. First, *Worrall et al*. [2013] have shown that the lowest bias estimation of annual flux is as follows:

$$F = KE(C_x)R_{\text{total}} \quad (1)$$

where R_{total} = the total precipitation in a year (mm/yr); $E(C_i)$ = the expected value of the sampled concentrations of x (mg/L); and K = unit conversion constant. The problem is then, what is the appropriate distribution for the concentration data from which an expected value can be derived? A visual inspection of the distribution of SRP in precipitation suggested that both Weibull and Gamma distributions might be appropriate and, because of the large number of values reported as zero, then data across the entire study period were considered rather than for individual years.

The second approach was to consider the sum of the amount in each collected sample and so for the n samples taken:

$$F = K\sum_i^n C_i R_i \quad (2)$$

where R_i = the total precipitation collected in period i (mm); C_i = the concentration in period i (mg/L), and K = unit conversion constant. However, as pointed out above, there are large numbers of samples where the SRP concentrations were reported as zero, below the detection limit. To overcome this problem, samples where the concentration was recorded as below the detection limit were not taken as zero but as half the detection limit, in this case 0.01 mg P/L and so concentrations were recorded as 0.005 mg P/L. For the calculation of the precipitation input of DOP, the assumption about concentrations below the detection limit was not necessary as there were no such cases. It was assumed that atmospheric particulate inputs were negligible.

2.3. P Exports

This study calculates the fluvial flux of P species at the catchment outlet (Trout Beck, TB) as a sum of the flux of a first-order stream entirely within the peat (Cottage Hill Sike: CHS) and the flux from the soils of the catchment (shallow soil water—SS). The difference between these fluxes represents in-stream processing within the catchment; therefore, this study takes a similar approach as that of *Worrall et al*. [2006, 2009]. In a deep-peat catchment it can be assumed that all the water leaving the catchment has come directly or indirectly through the surface layers of the peat; therefore, the flux from the soil can be calculated using shallow soil pore water concentrations in combination with the flow recorded at the catchment outlet for the same day as the soil water sample is taken. In this way the calculated flux represents the P flux as the water leaves the soil profile and the comparison between the export from SS, CHS, and TB. *Worrall et al*. [2003b] had considered the sources of water in this catchment and did identify a base-rich groundwater component at TB, but they did not consider P because concentrations were too low to include. To ensure that this assumption is reasonable, the conductivity of the water samples from SS, CHS, and TB were compared to ensure that the water mixing between these water bodies is as assumed.

As part of monitoring work carried out by the ECN, water samples were collected weekly from five stream sites though for this study only the samples from the catchment outlet (TB—Figure 2), the peat-hosted stream (CHS—Figure 2), and two weekly samples from six soils sites within the catchment (Figure 2) were considered. Soil water was sampled at two depths—10 and 50 cm below the surface; in this study the six samples from each depth were averaged. With relevance to this study samples were analyzed for SRP and DOC. Details of analysis can be found in *Sykes and Lane* [1996]. The DOC values were converted to DOP by reference to the C:P measurements described below.

Particulate concentrations of any form are not routinely measured at the site. However, POC flux for the site was assessed using the method of *Worrall et al*. [2003a] based on storm samples, i.e., sampling triggered on the storm hydrograph as opposed to the base flow. The sediment sampling program was used to construct a rating curve which in combination with flow records for the catchment outlet (TB) could be used to calculate a suspended sediment concentration at each flow. Suspended sediment flux measurements were converted to POC estimates based on the measurement of the carbon content of the collected suspended sediment and extended across the range of available flow records for the catchment. The POC values were converted to POP by reference to the C:P measurements described below. The POP flux as calculated by this method is the flux from the catchment outlet and not the flux as it leaves the soil profile and as such no estimate of in-stream losses or storage could be made.

To calculate all the fluvial fluxes of dissolved P, it was possible to utilize flow records recorded hourly at the catchment outlet (TB—Figure 2) where monitoring has been ongoing since October 1992. The fluvial fluxes of SRP and DOC were calculated using an interpolation method based upon equation (1):

$$F = KE(C_i)Q_{\text{total}} \tag{3}$$

where Q_{total} = the total flow in a year (m^3/yr); $E(C_i)$ = the expected value of the sampled concentrations (mg/L); and K = unit conversion constant (0.000001 for flux in tons). Where the expected value ($E(C_i)$) was based upon the fit of the Gamma distribution to the data from each year of sampling from the catchment outlet (TB); the peat-hosted stream (CHS); and the shallow soil water (SS).

For interpolation methods of flux estimation, i.e., equation (3), the major sources of error are the sampling frequency and the inherent error in the method used. *Worrall et al*. [2013] showed that for weekly sampling interpolation has a very low bias (6% for sampling frequency of 1 per week, 9% for sampling frequency of 1 per fortnight) and a high accuracy (1% at frequency of 1 per week and 2% for fortnightly). For extrapolation methods the error analysis depends on the fit of the equation between the determinand and the driving variable; error in the estimate of the POC was calculated by *Worrall et al*. [2009] as ± 86%.

2.4. Internal Transfers of Total P

The ECN monitoring only covers the precipitation, soil pore water, and some fluvial components; it does not include sampling or analysis of the plant and organic matter, or the suspended sediment. Therefore, in order to augment the ECN monitoring, estimate the DOP and POP fluxes and to help constrain internal transfers of P, samples of the dominant carbon pools were taken for CHNO and P analysis.

First, two locations in active, deep peat within the Cottage Hill Sike catchment were selected, and a peat core was taken to 1 m depth with a gouge auger from areas of the order of 10 m apart. The depth was selected to ensure coverage of both the acrotelm and catotelm [*Worrall et al*., 2012]. The collected peat cores were sampled in 2 cm depth increments from 0 to 20 cm depth from the peat surface, then 5 cm depth increments from 20 cm depth to 50 cm, and then one sample taken between 95 and 100 cm depth. Peat core samples were dried at 105°C overnight and checked for no further mass loss and their bulk density measured prior to further processing. Analysis of variance (ANOVA) was used to assess the differences between the two cores and with depth in the cores. Data were tested for normality prior to ANOVA, and no transformation was found necessary. The Tukey test was used for post hoc analysis between depths in the peat profile, the magnitude of the effects of each significant factor and interaction was calculated using the method of *Winer* [1971], and the results were expressed as least squares (or marginal) means.

Second, vegetation samples were collected from six quadrats within the catchment of the Cottage Hill Sike. The six quadrats were chosen to cover the three main plant functional groups present at the site: shrubs (dominantly *Calluna vulgaris*, henceforward referred to as *Calluna*); grasses and sedges (dominantly *Eriophorum* sp., henceforward referred to as grass/sedge); and mosses (including *Sphagnum* spp., henceforward referred to as mosses). In three of the quadrats the entire aboveground biomass was quantitatively recovered. For the three other quadrats, the total aboveground biomass was collected but separated by functional group. From within these quadrats, samples of litter and belowground biomass were recovered but not quantified. Quantitative biomass samples were dried to 105°C and weighed so that an estimate of total aboveground biomass and the contribution from the dominant functional plant groups could be estimated, while for the litter and belowground biomass these samples were just dried to 105°C. The dried samples were then homogenized and powdered as described below. In this way we were able to consider bulk measures of the vegetation organic matter pool and assess the contribution of its components. It would be expected that the aboveground biomass would be the weighted average of its components.

Finally, for the dissolved organic matter (DOM) and particulate organic matter (POM), samples of water from Cottage Hill Sike were collected monthly from January 2014 to June 2015 except for months where winter conditions precluded taking flowing water samples (23 samples in total). These samples were at least 25 L and the large volume required precluded sampling of soil water for obtaining DOM samples for P analysis. Furthermore, no samples of DOM were taken for the catchment outlet (TB) and so for the flux of DOM it was initially assumed that C:P was constant for DOM across the stream network. On return to the laboratory the samples were allowed to settle with water tapped off from above the sediment layer and then evaporated to dryness to collect the total dissolved solids. By using settling as means of separation, no arbitrary

filtration cutoff was being applied; rather, this study was defining DOM as being that component which was either colloidal or truly dissolved. The total dissolved solids for samples from Cottage Hill Sike would be expected to be predominantly organic matter, but the ash content (subsamples were ashed at 550°C and residual mass recorded) of the samples was analyzed, and all subsequent analysis were corrected so that all values are quoted on an ash-free basis. For the final 2 months of the DOM sampling, the settled sediment was recovered as a measure of the particulate organic matter (POM), dried to 105°C (overnight and checked for no further mass loss), and retained for subsequent analysis. As for DOM, it would be expected that suspended sediment from Cottage Hill Sike would be dominated by organic matter, but all samples were analyzed for their ash content and subsequent analyses adjusted for these values.

2.5. Sample Analysis

Triplicate samples of all the collected samples (aboveground and belowground vegetation, litter, peat soil, DOM, and POM) once dried to 105°C and were then milled to a submillimeter powder using a Spex 6770 Freezer Mill. The ground samples were then subject to CHN and O analysis on a Costech ECS 4010 Elemental combustion system with pneumatic autosampler. Computer software used was EAS Clarity (DataApex Ltd, Prague, Czech Republic). For both CHN and O setups, calibration curves of $r^2 > 0.999$ were created using acetanilide as the standard. Samples of acetanilide were included within each run as unknown samples to act as internal quality control checks. Each sample was analyzed in triplicate on the CHN setup and a further three times on O setup, and a mean calculated for C, H, N, and O. All samples were corrected for their measured ash content. For P analysis, dried and ground samples are redried for more than 8 h or overnight at 70 ± 5°C before subsamples are weighed for the analysis. Weights of about 100 mg were recorded using a four decimal place balance of dried sample in a 15 mL borosilicate (or quartz) tube, 1 mL of concentrated sulphuric acid was added to each sample, and then 0.4 mL of hydrogen peroxide (30%) was added twice. The tubes are then placed for 30 min on a heating block at 335°C. The tubes were removed from the block, and further hydrogen peroxide was added before the tubes were again placed on the heating block for 10 min, and the process is repeated until the digests are clear. The samples are made up to 15 mL with distilled water and then analyzed on a dual view inductively coupled plasma optical emission spectroscopy (Thermo ICap 6500).

2.6. Dry Matter and C Budget

The study site has been the subject of a number of studies into the carbon budget of its peat soils, and these carbon budgets can be used in conjunction with the elemental analysis to constrain the P budget. This study uses the most up-to-date and longest carbon budget information for the site [*Worrall et al*., 2009, 2012] and the dry matter budget of *Forrest* [1971]. The information from the carbon budget is used in a number of ways. The uptake of P by plants (plant uptake—Figure 1) can be estimated if the following are known: annual primary productivity, C:P ratio of the major plants, and the contribution of plant species to the overall productivity. The first is known from *Worrall et al*. [2009, 2012], and the second is known from the elemental analysis made on the collected vegetation samples. The last was obtained from biomass surveys of *Forrest* [1971] for this site at steady state; it has been assumed that that vegetation composition has not altered significantly over the time since that detailed study. The quantitative recovery of aboveground biomass and the test of its components meant that *Worrall et al*. [2016] in their analysis of oxidation states within this study catchment was able to confirm that the areas sampled within this study had aboveground biomass and composition within the ranges reported by *Forrest* [1971].

Worrall et al. [2009] proposed that the carbon budget of the site was:

$$100C_{pp} \Rightarrow 35C_R + 26C_{DOC} + 4C_{CH4} + 4C_{dissco2} + 9C_{POC} + 22C_{RES} \quad (4)$$

where C_x = carbon from the following uptake or release pathways, where x is PP = primary productivity, R = net ecosystem respiration, DOC = dissolved organic carbon; CH_4 = methane; dissco2 = dissolved CO_2; POC = particulate organic carbon; and RES = residual carbon stored in the soil. The residual carbon stored in the soils (C_{RES}) represents the long-term accumulation; in *Worrall et al*. [2012] this was assumed to be flux into the catotelm. *Worrall et al*. [2012] calculated these fluxes for the catchment for the period 1993 to 2009, and so this study used the methods developed in *Worrall et al*. [2009] combined with the ongoing hydroclimatic monitoring and water sampling to extend the period of estimated fluxes to the end of 2014 and so calculate C_{RES}. As long as the peat soils of the study are accumulating organic matter (C_{RES}), then that accumulation represents a flux of P into long-term storage (long-term storage—Figure 1). So if the C:P ratio

Table 1. Summary of Median Elemental Analyses of the Organic Matter Reservoirs Considered by the Study[a]

Organic Matter Pool	P Concentration (Mol P/100 g Organic Matter)	C:P	Median Stoichiometry
Calluna	0.173	769	$C_{1000}H_{1530}N_{10}O_{580}P_{1.3}$
Moss	0.055	2230	$C_{1000}H_{1560}N_{10}O_{650}P_{0.4}$
Sedge	0.047	2593	$C_{1000}H_{1560}N_{30}O_{640}P_{0.4}$
Aboveground biomass	0.069	1820	$C_{1000}H_{1540}N_{10}O_{610}P_{0.5}$
Litter	0.097	1300	$C_{1000}H_{1420}N_{30}O_{590}P_{0.8}$
Belowground biomass	0.068	1881	$C_{1000}H_{1480}N_{20}O_{580}P_{0.5}$
DOM	0.052	1856	$C_{1000}H_{1600}N_{50}O_{690}P_{1.2}$
POM	0.116	865	$C_{1000}H_{1120}N_{30}O_{740}P_{0.3}$
Peat (2 cm depth)	0.003	1904	$C_{1000}H_{1650}N_{20}O_{750}P_{0.6}$
Peat (95 cm depth)	0.001	3942	$C_{1000}H_{1650}N_{20}O_{750}P_{0.6}$

[a]The median stoichiometry is expressed relative to 1000 carbon atoms.

of the source material is known, then the equivalent amount of P can be estimated. The long-term storage of carbon is estimated from the average net carbon sink size over the period 1993–2014 and the appropriate C:P ratio from the measurements made upon the peat profile. In addition, as organic matter is transformed down the profile as it is buried and there could be release or uptake of P (organic matter turnover—Figure 1). *Worrall et al*. [2012] found that N was released through the peat profile as organic matter transforms. The release or uptake of P through the transformations in the profile was estimated based upon the change in C:P with the profile and fluxed of C down the profile.

Uncertainty in the each of these processes was calculated using the methods in *Worrall et al*. [2009].

3. Results

3.1. Elemental Analysis

All analyzed samples were ash corrected and results expressed as moles per 100 g and the C:P ratio (Table 1 and Figure 3). For the peat profile the P content varies from 0.001 mol P/100 g to 0.003 mol P/100 g (0.028 g P/100 g to 0.09 g P/100 g) with C:P ratio rising from 1327 to 4614. There were significant differences (P of no difference < 0.05) due to both depth in the peat profile and the P content between the two soil cores; however, the difference between the cores represented 9% of the original variance while the variation due to depth represented 69% of the original variance with 22% of the original variance due to error: there was no significant interaction between the depth profile of the two cores. The C:P ratio increased from a least squares mean value of 1904 ± 241 in the surface 2 cm of the peat profile to a least squares mean of 3942 ± 248 for the 95 to 100 cm interval. The P content decreased from 0.0022 ± 0.0002 mol P/100 g in the top 2 cm of the peat profile to 0.0012 ± 0.0002 mol P/100 g for the 95 to 100 cm depth increment. Post hoc analysis shows that the top 10 cm of the profiles are significantly different from the bottom 90 cm of the profile and the section from 45 to 100 cm depth. Figure 3 suggests that most of the decline is in the top 25 to 30 cm and composition being approximately constant over the bottom 70 cm of the profile, implying that the internal transfer of P occurs only at shallow depths. *Bridgham et al*. [1998] gives C:P values from 913 for ombrotrophic bogs to 189 for minerotrophic bogs. *Wang et al*. [2015] found that C:P ratios decreased from the top 50 cm to the bottom 50 cm of peat cores no matter from what type of peatland they were taken from (over 400 cores across Ontario): for these peat bogs the average C:P value increased from 892 in the top 50 cm to 1531 in the bottom 50 cm. *Hill et al*. [2014] report C:P ratios for fen peat of between 1506 and 2438. Given the measured P concentration and the bulk density of the peat cores, then the P content or stock within the top 1 m of the peat profile of the study site is between 48 and 55 g P/m^2.

In comparison, the aboveground and belowground biomass have very similar P contents but which are not as high as some of the peat surface soil samples (Figure 3). However, the composition of the individual plant functional types shows that although the P content of mosses and sedges/grasses is lower than for the aboveground biomass (0.0018 and 0.0016 mol P/100 g, respectively), the composition of the *Calluna* was 0.0056 mol P/100 g, i.e., the P content of the aboveground biomass is a mixture of the P contents of the individual plant functional types. Furthermore, the litter samples show a composition of 0.0032 mol P/100 g which appears to plot at the extreme shallow end of the peat soil P content profile. It could appear that litter has a greater P content than the vegetation, but it is likely that litter is dominated by litter from *Calluna* which

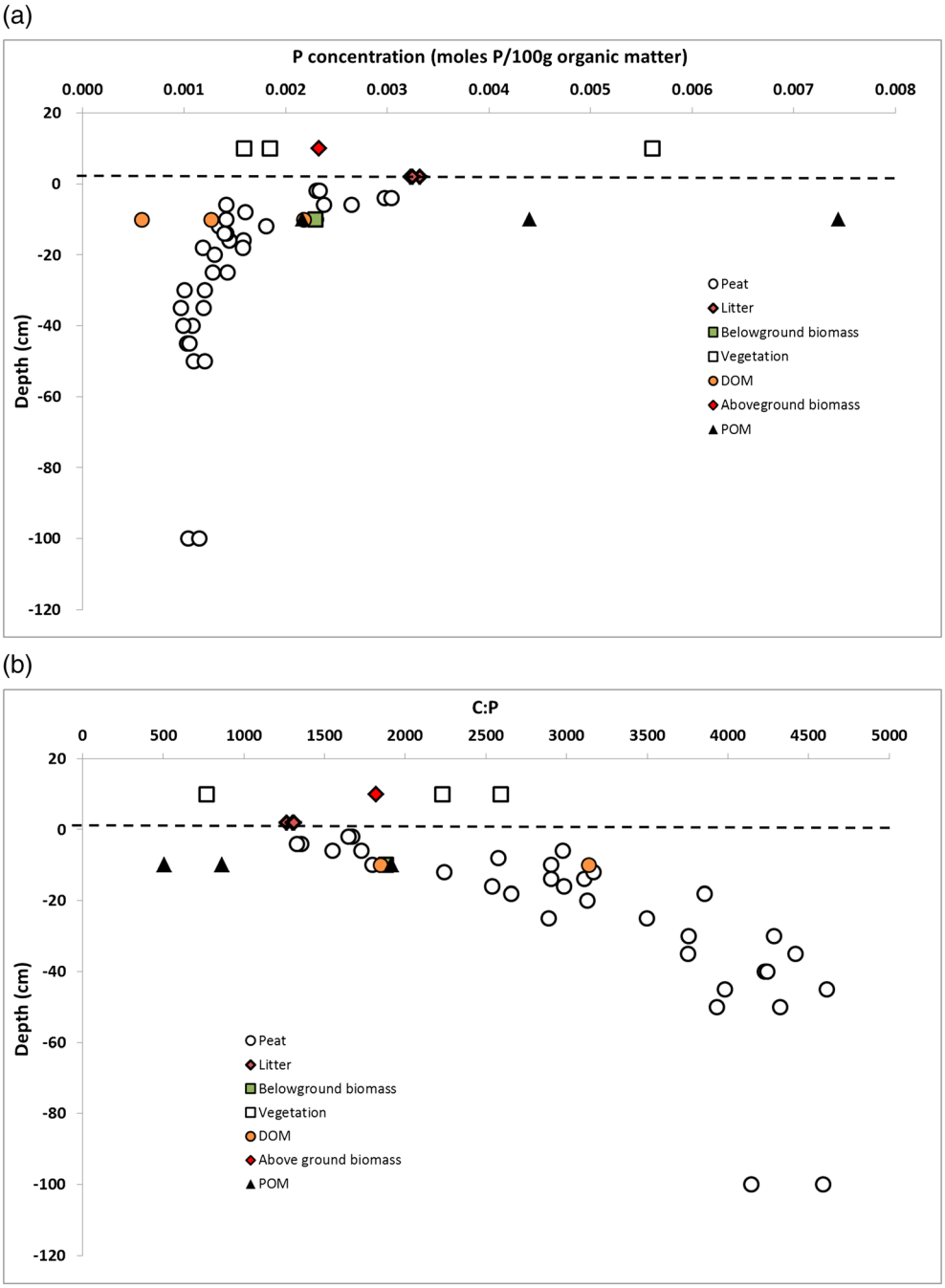

Figure 3. The (a) P content and (b) C:P ratios of the soil, DOM, POM, vegetation, and litter samples considered in this study. The samples of DOM and POM are given a nominal depth of 10 cm in the peat profile.

has already been shown to have the highest P concentration of any of the plant functional types. *Williams and Silcock* [2001] reported P concentrations in *Sphagnum* mosses as 648 mg P/kg (0.02 mol P/100 g). *Wang et al.* [2015] found bog vegetation to have C:P ratios between 347 and 924 and C:P for litter between 619 and 1051. Given the biomass measured in this study and the dry matter budget measured by *Forrest* [1971], it is possible to detail the biomass and litter stocks of P for this site (Table 2).

The range of P composition of the POM samples range from that of the litter to that of the peat soil at approximately 20 cm depth, but it still has the lowest C:P ratio and the second highest P concentration observed in

Table 2. The Stocks of P in the Biomass and Litter

	Median Stock	
Organic Matter Pool	Dry Matter (g/m^2)	P (g P/m^2)
Calluna	1547	2.68
Moss	100	0.05
Sedge	349	0.16
Aboveground biomass	1998	2.89
Belowground biomass	133	0.09
Total biomass	2131	2.98
Litter	589	0.57

this study (as high as 0.116 g P/100 g, 0.0044 mol P/100 g, C:P = 505). *Worrall et al*. [2016] suggested that on the basis of organic matter oxidation state, POM from the study catchment was a mixture of vegetation and peat from around 50 cm depth in the peat profile, and results here are consistent with that study. However, the very low C:P ratio is difficult to explain given the range of sources studied. In contrast, the P content of DOM varies from 0.01 to 0.05 g P/100 g (0.0006 to 0.0022 mol P/100 g), and a median C:P ratio of 1856. The low P concentration of DOM relative to P content of the peat soil, litter, or vegetation suggests that the production of DOM involves the removal of P just as it does of N [*Worrall et al*., 2012]. It is difficult to suggest a significant seasonal cycle in the P content of the DOM although the high values were all observed in the summer months. *Williams and Silcock* [2001] reported C:P ratios of DOM below *Sphagnum* as up to 1028, but *Rasanen et al*. [2014] recorded C:P ratios of DOM from boreal mires as high as 24157.

3.2. Measured Atmospheric Inputs

Over the period of the record there were 1214 measurements of SRP in precipitation samples of which 1122 were below detection limit (0.01 mg P/L). The expected value of the Gamma distribution was 0.002 mg P/L or 0.003 mg P/L if a Weibull distribution was fitted. When the original data were considered, the annual flux was between 0 and +159 kg P/km^2/yr, and there were 3 years in which there was no apparent input of P to the catchment. When the data were recalculated assuming recorded zero values were, in fact, 0.005 mg P/L (i.e., half the detection limit), this gave a flux of between +40 and +197 kg P/km^2/yr. Based upon the fit of the gamma distribution, the precipitation input of SRP varied from +26 to +128 kg P/km^2/yr; based upon the fit of a Weibull distribution, the precipitation input of SRP was from +30 to +150 kg P/km^2/yr. Thus, in neither case when a distribution was fitted to the modified data were any years found with zero input, and it is these estimates that were taken by preference giving a range of atmospheric input of SRP as +26 to +150 kg P/km^2/yr (Table 3).

The median DOC concentration of the precipitation was 1.2 mg C/L with a 5th to 95th percentile of 0.00 to 4.66 mg C/L. Based upon the ranges of C:P ratio observed for the sample DOM, the DOP in precipitation varies between +15 and +96 kg P/km^2/yr with a significant decline in this input over the time of the study—declining at a rate 1.9 kg P/km^2/yr. The expected value of the precipitation DOC concentration for the Weibull and Gamma distribution was 3.1 mg C/L and 4.6 mg C/L, respectively, which given the C:P ratio of the DOM means a precipitation flux of between +29 and +67 kg P/km^2/yr (Table 3 and Figure 4).

Table 3. The Fluxes of P at the Study Site as Detailed in Figure 1

Flux Pathway	Median (kg P/km^2/yr)	Range (kg P/km^2/yr)
Atmospheric deposition	99	60 to 160
Plant and litter uptake	90	19 to 162
Litter production	123	−52 to 192
Organic matter turnover	−28	−6 to −49
Fluvial flux from soil	−66	−49 to −111
Flux to long-term accumulation	18	3 to 32
Total budget	29	−6 to 72

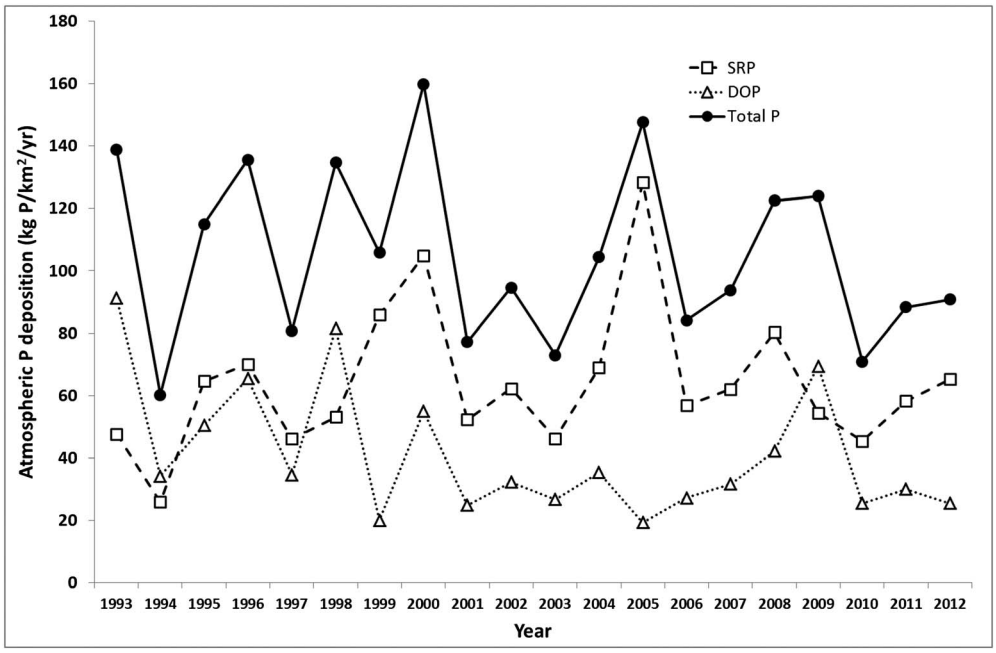

Figure 4. The time series of the atmospheric deposition of total P species at the soil source over the course of the study. For discussion of errors on estimates see text.

3.3. Measured Fluvial Outputs

The median concentration of DOC at CHS was 18.1 mg C/L with a 5th to 95th percentile range of 6.9 to 34.2 mg C/L; DOC export was between −17 and −50 t C/km^2/yr. Given the C:P values of the DOM, then the flux of DOP was between −17.8 to −61.6 kg P/km^2/yr. The distribution of SRP values for CHS shows that of the 1185 measurements, 1094 were below the detection limit of 0.01 mg P/L, and when raw data were used, the export of SRP from CHS was between 0 and −11.5 kg P/km^2/yr; in two of the years the flux was estimated as zero. When the assumption of half the limit of detection was used, then flux was between −5.3 to −18.3 kg P/km^2/yr. The expected value of the Gamma distribution of the SRP was 0.0031 mg P/L and for the Weibull distribution was 0.0023 mg P/L and, given such expected values, the flux of SRP at CHS would be between −3.5 to −6.0 kg P/km^2/yr and −2.6 and −4.4 kg P/km^2/yr, respectively.

The median concentration of DOC at TB was 8.3 mg C/L with a 5th to 95th percentile range of 4.1 to 20.4 mg C/L; DOC export was between −9.9 and −28.0 t C/km^2/yr. Given the C:P ratio of the DOM, the flux of DOP at TB would be between −2.3 and −6.3 kg P/km^2/yr. For the SRP concentration of the 1070 occasions it was analyzed since October 1992, there were 1042 where it was below the detection limit of 0.01 mg P/L. The flux of SRP at TB was between 0.00 and −7.52 kg P/km^2/yr; in 6 years of the study period the flux was predicted as 0.00 kg P/km^2/yr. When concentrations below the detection limit were assumed to be half the detection limit, then the flux was between −5.4 and −14.6 kg P/km^2/yr. Applying the Weibull and Gamma distributions gives expected values 0.0009 and 0.001 mg P/L which gives a flux of between −0.11 and −0.19 kg P/km^2/yr.

The median DOC concentration for SS was 21.3 mg C/L with a 5th to 95th percentile range of 15.2 to 34.8 mg C/L; DOC export was between −23.9 and −78.7 t C/km^2/yr which, given C:P ratio, gives a DOP flux between −20.8 to −75.8 kg P/km^2/yr (Table 3). For the SRP of the 534 analyses, 438 were below the detection limit of 0.01 mg P/L. For comparison, the soil water at 50 cm depth had only 11 out of 524 analyses that were above the detection limit of 0.01 mg P/L, i.e., SRP is most commonly giving a nominal flux of between 0 and −21.4 kg P/km^2/yr, with 2 years where zero flux is estimated or when censored then the flux is −5.7 and −29 kg P/km^2/yr. When distributions were fitted to the data, then the expected values were 0.007 and 0.012 mg P/l for the Weibull and Gamma distributions, respectively, which gives flux between −7.9 and −13.4 kg P/km^2/yr.

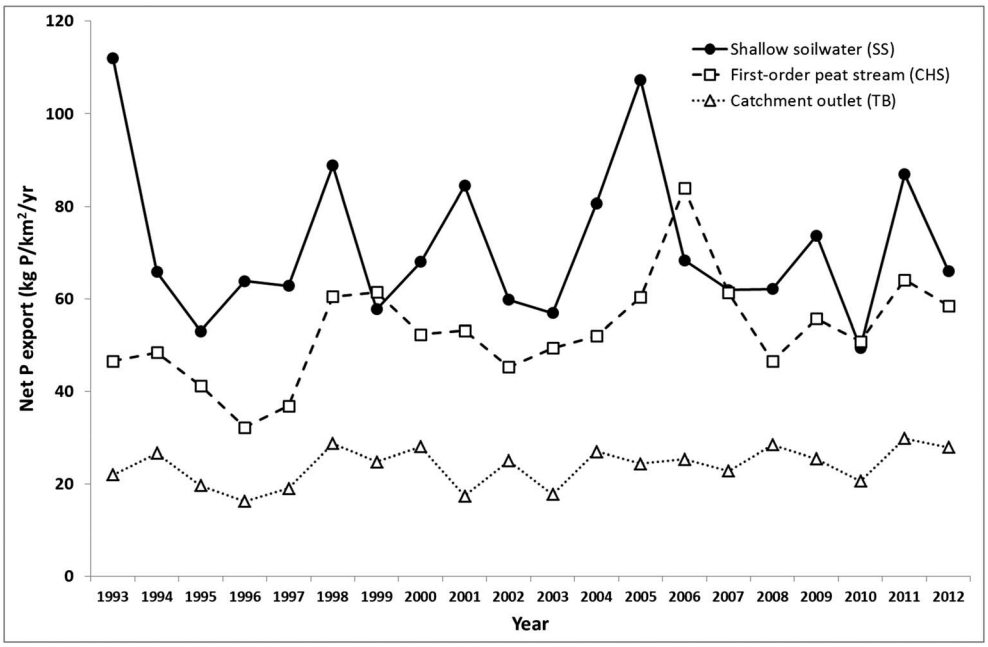

Figure 5. The time series of the fluvial export of total P over the course of the study. For discussion of errors on estimates see text.

The comparison between the DOP fluxes from SS and CHS shows that flux at CHS was between 29 and 129% of the flux as predicted from the SS samples. The DOC concentration of precipitation was on average 21 times less than the DOC concentration of the SS and 18 times more dilute than the DOC concentration in CHS. A comparison of the conductivity between the sample pools was as follows: precipitation (16.8 μS/cm, $n = 884$); SS (39.0 μS/cm, $n = 494$); CHS (40.7 μS/cm, $n = 1113$) suggesting that CHS water is dominated by SS water, and therefore, precipitation is mixing into the shallow soil water rather than finding flow paths to the stream network that bypass the peat profile. However, the fact that in three out of the 20 years of the study the flux estimated for CHS was greater than that predicted from the SS means that there is an additional source of dissolved organic matter which could be in-stream production. The median loss rate of DOP between SS and CHS was 30% which equates to a release of −11 kg P/km^2/yr. Between CHS and TB, the median annual loss rate was 85% (−26 kg P/km^2/yr), and so the loss rate between SS and TB was 90% which equates to a loss of −33 kg P/km^2/yr (Table 3). It should always be remembered that C:P values were only ever measured for CHS, and so there may be a systematic change in C:P ratio of DOM across the study catchment. Comparing the SRP exports based upon the assumption that SRP concentrations below the detection limit have a concentration of half the limit of detection, then the SRP export increases across the catchment with the export at TB being 113% of the SS export and an increase of 1 kg P/km^2/yr. When the fitted Gamma distributions were used, then the SRP export decreased across the catchment with the export at TB being only 14% of that predicted from SS (i.e., an average 86% loss) or a source of 9.6 kg P/km^2/yr.

The estimated POP flux at TB from over the study period was between −13 and −22 kg P/km^2/yr. No estimate of the in-stream loss of POP could be made, and so the flux at TB is taken as the flux from the soils to the stream network (Table 3).

The total dissolved fluvial flux of P (Figure 5) from SS was between −22 and −95 kg P/km^2/yr dropping to between −3.5 and −8.0 kg P/km^2/yr for TB. At CHS there was a significant increase in the total dissolved phosphorus over the course of the study increasing at a rate of 0.7 kg P/km^2/yr; there was no significant trend over time for either SS or TB. The total fluvial P flux (dissolved + particulate P) from the soil was between −49 and −111 kg P/km^2/yr (median = −65.9 kg P/km^2/yr), but by TB this had decreased to between −16.2 to −29.8 kg P/km^2/yr (median = −24.9 kg P/km^2/yr).

3.4. Internal Transfers

The mean and standard deviation of the C:P ratio of typical vegetation types and litter samples are given in Figure 3. Annual primary productivity measured for the site varied from +293 to +34 t C/km^2/yr [*Worrall et al.*,

Figure 6. The total P budget of the time course of the experiment. For discussion of errors on estimates see text.

2009] giving an uptake of P into the standing biomass of +19 and +162 kg P/km^2/yr (plant and litter uptake—Figure 1). Given that litter will be dominated by production from *Calluna*, litter production represents a source of P, i.e., litter will not uptake P as proposed in Figure 1. *Forrest* [1971] estimated that *Calluna* primary production represented 72.9% of the annual primary production and that the annual litter production for the site was +108 t C/km^2/yr. In turn this would mean that it represents a source of P of +123 kg P/km^2/yr but with a range of between +192 and −52 kg P/km^2/yr (litter production—Figure 1)—there is a chance that litter production is a sink of P.

The increase in C:P with depth implies a release of P within the top 30 cm of the peat profile (organic matter turnover—Figure 1). An estimate of the amount of carbon taking that transition on an annual basis can be made from the estimate of the carbon budget of the catchment as reported in *Worrall et al*. [2009]—between −11 and −95 t C/km^2/yr. The P release from organic matter making this transition therefore varied from −6 and −49 kg P/km^2/yr. This means that the P demand of the annual primary production could be met from the turnover of the litter and organic matter in the top 30 cm of the peat profile.

The transition into long-term storage is presented by the flux of organic matter from the 30 cm depth to the 100 cm depth (C_{RES}—equation (4)). Given the variation in C_{RES} over the study period and the C/P ratio of the peat below 30 cm depth in the profile, then the long-term accumulation is between +3 and +32 kg P/km^2/yr.

3.5. Total P Budget

The overall budget of the peat soils of the catchment is the difference between the total atmospheric inputs, and the total fluvial losses and as such this budget varies from −5.6 to +71.7 kg P/km^2/yr where a negative value represents a net loss; over the 20 years of the study the median budget was +29.4 kg P/km^2/yr. There was no significant trend in the overall budget, and of the 20 years of budget estimates, there was a net loss in 2 years and a net gain in 18 years (Figure 6). The median budget is within the range estimated from the long-term storage of organic matter predicted from the peat profile.

4. Discussion

The greatest limitation has been the very low concentrations of P in the sampled organic matter reservoirs. When raw data were used, then unreasonable variation in flux and export estimates occurred, including the estimation that in some years the export was zero. The alternative approach of this study was to consider the

distribution of the data, but even so the extremely skewed nature of the distribution of SRP concentration meant that although there in some cases over 1000 data points, only 5% or less are greater than the detection limit. However, the study does suggest that the blanket assumption of a single multiplicative approach [e.g., *Palarea-Albaladejo and Martin-Fernandez*, 2013] would be weak and even the lognormal distribution approach of *Helsel and Gilliom* [1986] would also be inappropriate here. When the Gamma or Weibull distributions are fitted to the data in this study, then the expected values of the SRP concentrations are less than half the detection limit.

This study has assumed that it is sufficient to represent the composition of DOM between the soil water (SS); the first-order peat stream (CHS); and the catchment outlet (TB) with C:P based only on samples from CHS. Results here suggest 80% loss across the catchment but at a C:P ratio based on sampling from the intermediate DOM reservoir, i.e., CHS—the first-order peat stream. However, to explain such a large loss in terms of changes in the composition of DOM, then the C:P ratio at TB would have to be higher than that at CHS, and the C:P ratio would have to be lower in the soil water (SS). Previous studies have predicted high removal rates for DOC for the streams of this site: *Worrall et al*. [2006] measured a removal rate of 35% across the catchment, and *Moody et al*. [2016] calculated a 10 year average loss rate across the catchment as 29% at an average in-stream residence time of 4.33 h, i.e., lower removal rates than predicted by the approach above. Given the removal rate predicted for the DOC, then it may be that C:P does increase through the catchment, in which case it would imply that C:P ratio of DOM does increase through the catchment. If that were the case, then the primary driver for DOM removal in the streams of the study catchment is not as a nutrient source but as an energy source. *Rasanen et al*. [2014] found that adding inorganic P to water samples from boreal mires did not increase the mineralization of DOM.

The above approach has assumed no role for land use or land management. There are number of land uses common in British upland peats that may alter the peatland budget. In UK upland peat ecosystems vegetation management by burning is common practice [*Yallop et al*., 2009]. *Rosenburgh et al*. [2013] considered the change in soil and plant nutrients across sites after burning of *Calluna vulgaris* and found that although there was significantly increased N saturation after burning, there was no consistent change relative to total or available P.

Many land management techniques in upland control the water table, either lowering it for drainage reasons or raising the water table for purpose of restoration. *Macrae* et al. [2013] found that a 20 cm lowering of the water table on a Quebec peatland led to no change in the P mineralization rate nor the water-extractable SRP concentration. P is commonly added to peatlands as part of restoration [e.g., *Groeneveld et al*., 2007] where the fertilization means that vascular plants and pioneer mosses act to stabilize the soil surface and create a microclimate for Sphagnum mosses. *Sottocornola et al*. [2007] recommend fertilization at rates of up to +37 kg P/km^2.

Sheep grazing is common and grazing densities can be as high as 1 ewe/ha [*Natural England*, 2010a, 2010b], although for our study site the present grazing intensity is nearer 0.1 ewes/ha. *Haygarth et al*. [1998] considered the P budget of a Scottish hill farm (including peat soils) and suggested an accumulation of +28 kg P/km^2/yr, but the study did not consider the removal of P in the skeletons of the sheep. *Worrall and Clay* [2012] modeled the carbon and greenhouse budget of upland sheep. The calculation of nutritional requirement of sheep assumed that each ewe had a lamb and that ewes ceases lactating 6 weeks after birth and that the lamb requires 0.8 kg dry matter per day. Further, it was assumed that on average a lamb has to produce 58 kg of weight from grazing and 22 kg from lactation. The majority of P supplied to livestock would go to develop a skeleton and so the fate of that skeletal material is crucial. Within each animal the proportion of meat, fat, and bone was taken as (67.5: 7.5: 22.5, respectively by weight) [*Kempster et al*., 1986], and P content of all produced materials was based on values from *McCance and Widdowson* [2002]—17% P in bone, 0.0011% in fat, and 0.00017% in meat. Therefore, in each lamb there would be 3.16 kg P/ca, and so at 1 ewe/ha the flux of the offtake due to lambs would be 316 kg P/km^2/yr. Within the North Pennines region, the latest guidelines being used by Natural England advisors come from *Natural England* [2010a]. Recommended maximum annual average stocking rates are suggested as 0.44 ewes/ha to maintain favorable condition or 0.23 ewes/ha to restore to favorable condition. For a farm in the North Pennines, the stocking densities have declined, prior to 2004—0.94 ewes/ha, between 2004 to 2009—0.63 ewes/ha; and 2009 to date—0.56 ewes/ha under a Higher Level Stewardship [*Natural England*, 2010b] agreement; however, at high altitude this can drop to 0.23 ewes/ha which gives an offtake (the net annual amount that actually leave the ecosystem) of 72 kg P/km^2/yr. For the study site the offtake would be 31.6 kg/km^2/yr which is within the range of the P sink predicted for the catchment predicted from the contemporary fluxes and the long-

term accumulation. It would be difficult to see how a peat ecosystem could continue to thrive with such an offtake of nutrient. The offtake of nutrient will come from the biomass and would result in reduced litter production and therefore a reduced pool of material from which P could be recycled which in turn means that more organic matter would need to be turned over to provide the P requirement and so limit carbon storage.

5. Conclusions

The study has shown that the ecosystem is on average a net sink of P of +29.4 kg P/km^2/yr over a 20 year period, but for 2 years during the study period the site was a net source of total P. The budget estimate is in line with the long-term composition of the peat profile where the estimated long-term sink is between 3 and 32 kg P/km^2/yr. In this P-limited ecosystem, P is rapidly turned over in the top 30 cm of the peat profile and rapidly lost from the dissolved phase in the first-order streams of the catchment.

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